Preparation and Characterization of Well-defined Co/SiO_2 Spherical Catalyst for Fischer Tropsch Synthesis (FTS)

by

Saiful Bahari bin Saleh

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2009

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

(AP Dr. Noor Asmawati M. Zabidi)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SAIFUL BAHARI BIN SALEH

ABSTRACT

This research project, which falls under the scope of catalysis, is conducted with the aim to study the preparation methods of cobalt nanocatalysts on SiO_2 support for the Fischer Tropsch synthesis (FTS). Variables such as the metal loading, ageing time and calcinations temperatures were studied during the catalysts preparation. Ammonia deposition and impregnation methods were used to synthesize the Co/SiO_2 catalyst. Co/SiO_2 catalyst were characterized using Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) and BET Surface Area Analyzer. The white silica spheres, which were prepared using Stober method gave a result of $198m^2/g$ for BET surface area. The cobalt metal was attached to silica spheres which have BET surface area of $61m^2/g$ at 2, 3 and 5wt% loadings. EDX analysis showed the presence of Si, O and Co elements in the catalyst. A rough statistical analysis on the TEM images from 5wt% impregnated catalyst showed cobalt particles with diameter ranging from 11 nm to 17 nm deposited on silica spheres. The average diameter of SiO_2 sphere is 130nm. The inconsistencies of metal attachments on the silica for impregnation method seem to be due to inefficient stirring during preparation. XRD analysis indicates the amorphous nature of the catalyst.

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This project would not have been possible without the assistance and guidance of certain individuals and organization whose contributions have helped in its completion.

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ABBREVIATIONS AND NOMENCLATURE

Co/SiO_2	Cobalt catalyst with support of silica sphere
GTL	Gas to liquid
FTS	Fischer Tropsch Synthesis
SASOL	South African Synthetic Oils
BASF	Baden Aniline and Soda Factory
Syngas	Synthesis gas
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
EDX	Energy Dispersive X-ray
$Co(NO_3)_2.6H_2O$	Cobalt (II) Nitrate Hexahidrate
TEOS	Tetraethylorthosilicate
NH_4OH	Ammonia solution
IUPAC	International Union of Pure and Applied Chemistry
UTP	Universiti Teknologi PETRONAS

CHAPTER 1
INTRODUCTION

1.1 Background Study

Due to the rising cost of petroleum, the availability of stranded natural gas reserves and politically driven and environmental motivations to decrease the flaring of natural gas, there is increasing industrial activity aimed at improving gas-to-liquids (GTL) technology. At the heart of the process is the Fischer Tropsch synthesis (FTS) reaction. The current commercial catalyst of choice for slurry phase processes is cobalt/alumina, where the cobalt loading is very high at 33%. SASOL has reported that the high loadings are necessary to achieve high activity and stabilize the catalyst against deactivation processes. [1]

Cobalt catalysts for FTS were first discovered more than 90 years ago. Indeed, the production of liquid hydrocarbons over cobalt catalysts was first reported in 1913 granted to BASF. In the subsequent nine decades, catalysts technology has advanced from simple moderately active Kieselguhr-supported cobalt to sophisticated, high activity and highly optimized cobalt catalysts supported on carefully design alumina, silica and promoted with noble metals and basic oxides. Advances in cobalt catalyst design can be conveniently discussed in the context of five historical periods:

i. 1902 – 1932 → Discovery
ii. 1933 – 1954 → Commercial development of cobalt and iron catalysts
iii. 1950 – 1985 → The Iron Age
iv. 1973 – 1990 → Rediscovery
v. 1990 – present → GTL and return to cobalt

During the period, catalyst design has evolved from trial and error art based experimentally reactor test of activity and selectivity to a scientific, nanoscale design founded on activity structure relationships and computerized theoretical models. [2]

1.2 Problem Statement

Fischer Tropsch synthesis (FTS) is currently an economically attractive process for the production of environmentally friendly diesel fuel. Supported cobalt catalysts are the system of choice for the FTS due to the high per pass conversion, low water gas shift activity, and paraffinic nature of the resulting synthetic crude. The catalytic behavior of the catalysts is strongly influenced by the morphology and the preparation method. [3]

The problems with cobalt catalysts as used in FTS are that they are relatively expensive as compared to iron and require high metal dispersion and a long life to remain economically feasible. Hence, for the optimum cobalt usage, detail understanding of the sensitivity of the FTS activity, selectivity and deactivation rate to the cobalt crystallite size is imperative.

Past researchers conclude that the FTS is a structure insensitive reaction that is there are no major changes in activity and selectivity over a wide crystallite size range. However, the oxidation of cobalt to cobalt oxide by means of water has long been postulated as a major deactivation mechanism during FTS and is thought to be related to cobalt crystallite size distribution.

To date, no study has dealt specifically with the influence of crystallite size on the oxidation behavior of cobalt. Therefore, this project is designed to prepare and characterize well-defined cobalt catalysts with the support of silica spheres. The correlation between preparation methods and the final physical properties of the catalysts will be studied. In a long term goal, it is also aimed to develop the best

procedures for producing cobalt catalysts with optimum dispersion to increase the effectiveness of the FTS process. Ammonia deposition and impregnation have been identified as potential methods to prepare the catalysts with support of silica.

1.3 Project Objectives

1. To prepare cobalt catalysts with support of silica spheres, Co/SiO_2

   Two main stages in the project are preparations and characterizations of the catalysts. The preparations stage involves the silica support and catalysts preparations. The silica is prepared by following the Stober method and the catalysts are prepared according to ammonia deposition and impregnation methods.

2. To characterize the prepared cobalt catalyst with support of silica spheres, Co/SiO_2

   After preparation stage, the cobalt catalysts with silica support are characterized for related parameters. Measurements like Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and X-Ray Diffraction (XRD) will be involved in the characterization stage.

3. To correlate the catalysts preparation method and their physical properties after preparations

   After completing the characterization stage, the results for different cobalt loadings are compared to each other in order to understand the physical properties of the catalysts and correlate them with the preparation methods.

1.4 Scope of Study

This project mainly involved study of catalysts and its behavior under the scope of catalysis. Catalysis is defined as the process in which the rate of chemical reaction is increased by means of a chemical substance known as a catalyst. The productions of most industrially important chemicals involve the usage of catalysts. For example, in the production of environmentally diesel fuel from syngas by FTS, the cobalt is used as the catalyst because it results in a high per pass conversion. [5]

For this project, cobalt catalysts with support of silica spheres, Co/SiO_2 are prepared by focusing on two methods; the ammonia deposition and impregnation methods. During the preparation stage, variables to be investigated are the metal loading, ageing time and calcinations temperature. Silica spheres are prepared first using ammonia solution, absolute ethanol and tetraethylorthosilicate. Different cobalt loadings on the silica supports are then prepared by ammonia deposition and impregnation methods.

The synthesize nanoparticles of cobalt catalysts from preparation stage are characterized in terms of particle size, surface area, porosity and reducibility. The characterization stage involves analytical equipments such as Transmission Electron Microscopy (TEM), Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and BET Surface Area Analyzer.

CHAPTER 2
LITERATURE REVIEW

2.1 Background of Fischer Tropsch Synthesis (FTS) [4]

The twentieth century coal to petroleum, or synthetic fuel industry evolved in three stages:

i. Invention and early development of the Bergius coal liquefaction (hydrogenation) and Fischer Tropsch synthesis (FTS) from 1910 to 1926.
ii. Germany's industrialization of the Bergius and FT processes from 1927 to 1945.
iii. Global transfer of the German technology to Britain, France, Japan, Canada, the United States, South Africa and other nations from 1930's to 1990's.

Germany was the first of the industrialized nations to synthesize petroleum when Friedrich Bergius (1884 - 1949) in Rheinau-Mannheim in 1913 and Franz Fischer (1877 - 1947) and Hans Tropsch (1889 - 1935) at the Kaiser Wilhelm Institute for Coal Research (KWI) in Mulheim, Ruhr, in 1926 invented processes for converting coal to petroleum. Their pioneering researches enabled IG Farben, Ruhrchemie and other German chemical company to develop a technologically successful synthetic fuel industry that grew from a single commercial size liquefaction plant in 1927 to twelve (12) coal liquefaction and nine (9) FT commercial size plants that in 1944 reached a peak production of 23 million barrels of synthetic fuel.

Britain and Germany had the most successful synthetic fuel programs. The others were either smaller scale operations, such as France's three demonstration plants (two coal liquefaction and one FT), Canada's bitumen liquefaction pilot plants, and Italy's two crude petroleum hydrogenating (refining) plants, or technological failures as were Japan's five commercial size plants (two coal liquefaction and three

FT) that produced only about 360,000 barrels of liquid fuel during the World War II years.

Germany has virtually no petroleum deposits. Prior to the twentieth century this was not a serious problem because Germany possessed abundant coal reserves. Coal provided for commercial and home heating; it also fulfilled the needs of industry and the military, particularly the navy. In the opening decade of the twentieth century, Germany's fuel requirements began to change. Two reasons were especially important. First, Germany became increasingly dependent on gasoline and diesel oil engines. The appearance of automobiles, trucks and the airplanes made a plentiful supply of gasoline essential. Moreover, ocean going ships increasingly used diesel oil rather than coal as their energy source. Second, Germany's continuing industrialization and urbanization led to the replacement of coal with smokeless liquid fuels that not only had higher energy content but were cleaner burning and more convenient to handle.

Petroleum was clearly the fuel of the future, and to insure that Germany would never lack a plentiful supply, German scientists and engineers invented and developed two processes that enabled them to synthesize petroleum from their country's abundant coal supplies and to establish the world's first technologically successful synthetic liquid fuel industry. Bergius in Rheinau-Mannheim began the German drive for energy independence with his invention and early development of high pressure coal hydrogenation in the years 1910-1925. Bergius crushed and dissolved a coal containing less than 85% carbon in a heavy oil to form a paste. He reacted the coal oil paste with hydrogen gas at high pressure (P = 200 atm) and high temperature (T = 400°C) and obtained petroleum like liquids. Bergius sold his patents to BASF in July 1925, and from 1925 to 1930 Matthias Pier (1882 - 1965) at BASF made major advancements that significantly improved product yield and quality. Pier developed sulfur resistant catalysts, such as tungsten sulfide and separated the conversion into two stages, a liquid stage and vapor stage.

A decade after Bergius began his work, Fischer and Tropsch at the Kaiser-Wilhelm Institute invented a second process for the synthesis of liquid fuel from coal. Fischer and Tropsch reacted coal with steam to give a gaseous mixture of carbon monoxide and hydrogen and then converted the mixture at low pressure (P = 1-10 atm) and temperature (T = 180-200°C) to petroleum like liquid. Fischer and his co-workers in the 1920-1930 developed the cobalt catalysts that were critical to the FTS success, and in 1934 Ruhrchemie acquired the patent rights to the synthesis.

Synthesis gas can also be created from natural gas, and this is less costly than from coal. Since 1993, Shell in Malaysia (Bintulu) and PetroSA in South Africa (Mossel Bay) have been operating industrial Fischer Tropsch facilities, which produce liquid fuels from synthesis gas which comes originally from natural gas (Gas to Liquid, GTL). A third similar plant is being built by SASOL and Qatar Petroleum in Qatar in the Persian Gulf. The number of GTL facilities is increasing worldwide and most of them are to use the Fischer Tropsch Synthesis (FTS).

Given the quick rise in the price of crude oil and the dramatic consequences of hurricane season for American oil production and processing, the United States (US) is rethinking how it deals with its large domestic coal inventory. In 2006, the first US coal to diesel (CTL) production facilities is planned in Gelberton, Pennsylvania. It uses indirect coal liquefaction (CTL) via coal gasification and Fischer Tropsch Synthesis. Two further similar US projects are following after that. China too, has been investing in CTL technology using indirect Fischer Tropsch Synthesis

2.2 The Reaction [4]

The Fischer Tropsch synthesis (FTS) is a catalyzed chemical reaction in which synthesis gas or syngas, a mixture of carbon monoxide and hydrogen is converted into liquid hydrocarbons of various forms. The most common catalysts used are cobalt and iron, although nickel and ruthenium have also been used. The principle

purpose of the process is to produce a synthetic lubrication oil or as synthetic fuel. The fuel is used to run vehicles such as trucks, cars and aircraft engines.

The FTS involves a variety of competing chemical reactions, which lead to a series of desirable products and undesirable byproducts. The most important reactions are those resulting in the formation of alkanes. These can be described by chemical equations of:

$$(2n+1)H_2 + nCO \rightarrow CnH\,(2n+2) + nH_2O$$

'n' is the positive integer and setting n=1 will result in formation of methane. In the case of mass production, process conditions and catalyst composition are usually chosen, so as to favor higher order reactions and minimize formation of methane. Most of the alkanes produced tend to be straight chained, although some branched alkanes are also formed. Usually, only relatively small quantities of non alkane product are formed.

FTS is usually operated at the temperature range of 150 – 300°C. Operating FTS at higher temperatures will lead to faster reactions, higher conversion but favor formation of methane. Higher operating pressure may lead to higher conversion rates and also tend to produce long chained alkanes, both of which are desirable. For optimum result, temperature usually maintained at low to middle part of the range and pressure between 1 – 10 atm.

2.3 The Catalysts [5]

The Fischer Tropsch synthesis (FTS) has shown to be catalyzed by certain transition metals, with cobalt, iron and ruthenium results in the highest activity. Among them, cobalt catalysts are the most preferred catalysts for FTS because of high activity and high selectivity to linear hydrocarbons, low activity to water gas shift reaction, more

stable toward deactivation by water and lower cost compared to ruthenium. Nickel can also be used, but favor methane formation.

In order to achieve high surface active sites, cobalt precursors are dispersed on porous carriers, with silica and alumina. A drawback of these support materials is their reactivity toward cobalt, which during preparation of catalysts result in formation of mixed compounds that are reducible only at high reduction temperatures.

Unlike cobalt which remains in the metallic state during synthesis, iron catalysts for FTS tend to form a number of chemical phases, including various iron oxides and iron carbides during the reaction. Control of these phase transformations are important in maintaining catalytic activity and preventing breakdown of the catalyst particles.

The FTS catalysts are sensitive to the presence of sulphur containing compounds among other toxins. The sensitivity of the catalyst to sulphur is higher for cobalt based catalysts than iron. The following table shows comparisons between cobalt and iron catalysts for FTS in few related parameters.

Table 2.1: Comparison of Cobalt and Iron FTS Catalysts

Parameter	**Cobalt Catalysts**	**Iron Catalysts**
Cost	More expensive	Less expensive
Lifetime	Resistant to deactivation	Less resistant to deactivation (coking, carbon deposit, iron carbide)
Activity at low conversion	Comparable	
Productivity at high conversion	Higher. Less significant effect of water on the rate of carbon monoxide conversion	Lower. Strong negative effect of water on the rate of carbon monoxide conversion
Maximum chain growth probability	0.94	0.95
Water gas shift reaction:	Not very significant,	Significant

$CO + H_2O \rightarrow CO_2 + H_2$	more noticeable at high conversions	
Maximum sulfur content	< 0.1 ppm	< 0.2 ppm
Flexibility (temperature and pressure)	Less flexible. Significant influence of temperature and pressure	Flexible. Methane selectivity is relatively low even at 613K
H_2/CO ratio	≈2	0.5 – 2.5
Attrition resistance	Good	Not very resistant

2.4 Catalyst Specifications [4]

In order to progress from prototype catalysts to a version capable commercial scale production, not only does the catalyst preparation route need to be specified in considerable detail but also, the specification of the finished catalyst needs to be defined. A set of physical and chemical characteristics need to be determined which fully define the catalysts and then, for each of these characteristics an acceptable value, or more usually a range of values, is set. Physical parameters used to specify the finished catalyst are as follows:

- BET surface area as measured by nitrogen porosimetry
- Mean pore diameter
- Skeletal density
- Mercury intrusion volume
- Mercury pore area
- Mercury particle density
- Mercury skeletal density
- Extrudate diameter, length
- Attrition resistance and bulk crush strength

The definition of the chemical specification is more complex. For instance not only does the cobalt loading and the levels of numerous elements, some present in only in trace amounts, need to be specified but also measures of the state of the cobalt oxide are also required. Techniques used to 'fingerprint' the active phases include X-ray diffraction (XRD) to determine crystallite phase sizes and Temperature Programmed

Reduction (TPR). The TPR experiments are run with hydrogen and conditions are chosen to produce a characteristic trace with sharp peaks. The temperatures corresponding to these peaks are indicative of the 'reducibility' of the cobalt and prove to be strongly correlated with catalyst performance under process conditions. Electron microscope techniques are used to determine the distribution of the active phase throughout the extrudates to ensure it was uniform. The catalyst specifications prove to be essential for moving into the next phase of development.

2.5 Catalyst Characterizations

2.5.1 Transmission Electron Microscope (TEM)[11]

The transmission electron microscope (TEM) operates on many of the same optical principles as the light microscope. The TEM has the added advantage of greater resolution. This increased resolution allows us to study ultra structure of organelles, viruses and macromolecules. Specially prepared materials samples may also be viewed in TEM. The light microscope and TEM are commonly used in conjunction with each other to complement a research project.

The electrons are very small and easily deflected by hydrocarbons or gas molecules, it is necessary to use the electron beam in a vacuum environment. A series of pumps are used to accomplish an adequate vacuum for this purpose. Rotary pumps are the first in the series. They are also called the 'roughing pumps' as they are used initially lower the pressure within the column through which the electron must travel at Hg range. Diffusion pumps may achieve higher vacuums (in the 10-5 mm Hg range) but must be backed by the rotary pump. The diffusion pump also maintains pressure. In addition a Turbo, Ion or Cyro pumps backed by the preceding pumps may be used when an even greater vacuum is required.

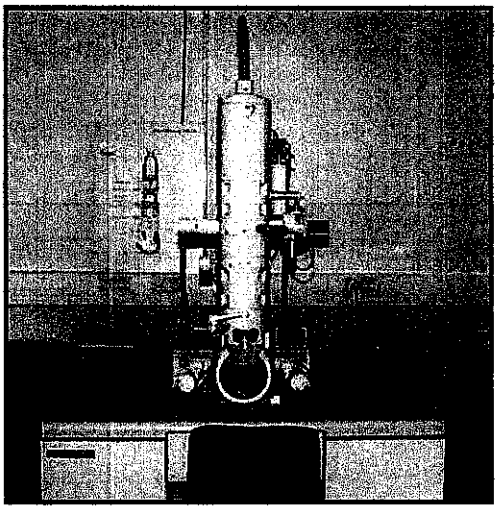


Figure 2.1: Transmission Electron Microscope (TEM) Equipment [12]

2.5.2 Scanning Electron Microscope (SEM) [13]

The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electron s and X-ray are ejected from the sample. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a similar to a television screen. This produces the final image.

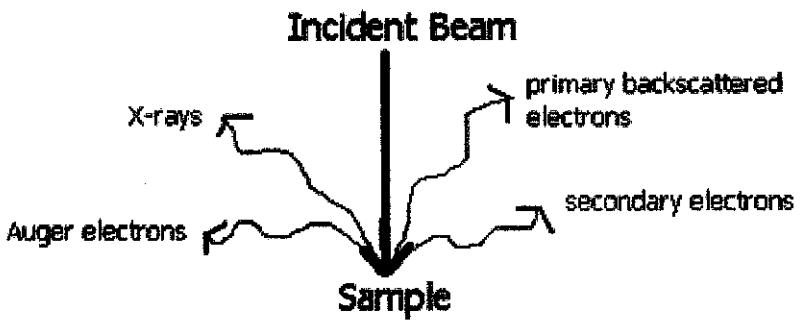


Figure 2.2: Mechanism of Scanning Electron Microscope (SEM)

The signals derived from interactions between electron and sample reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over selected area of the surface of the sample, and a 2D image is generated that displays spatial variations in these properties. Area ranging from approximately 1cm to 5microns in width can be imaged in SEM with magnification ranging from 20X to approximately 30000X, spatial resolution of 50 to 100nm. The SEM also capable of performing analysis of selected points' locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions, crystalline structure and crystal orientation

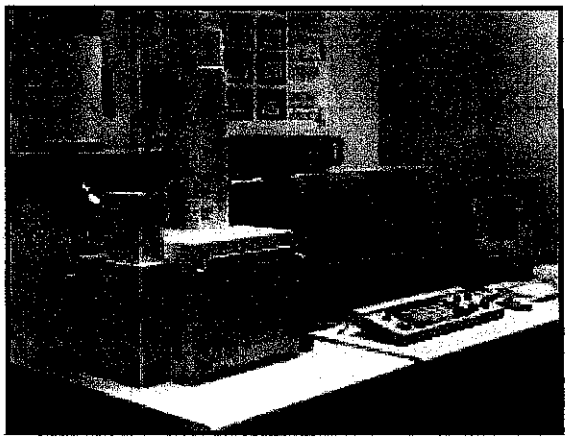


Figure 2.3: Scanning Electron Microscope (SEM) Equipment

2.5.3 Energy Dispersive X-Ray Analysis (EDX) [14]

Analytical techniques applied in transmission and scanning electron microscopy can provide valuable information of a specimen additional to its ultrastructure. The distribution and frequency of different element in cells, tissues or solid slates is of a major importance. The analysis of the elements is mostly done by energy dispersive x-ray analysis (EDX) using a dedicated detector. Elemental distributions can be determined either in a SEM (bulky specimens) or in TEM (thin, electron transparent specimens).

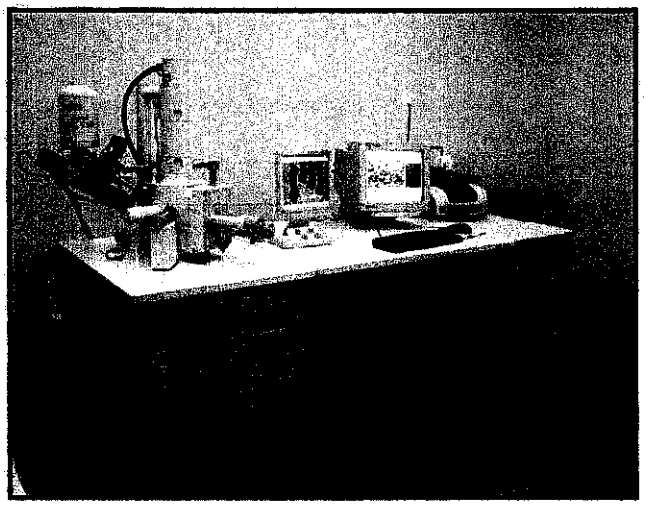


Figure 2.4: Energy Dispersive X-Ray (EDX) Equipment

EDX requires a high energy primary electron beam in the microscope. Electrons collide and knock off electrons of atoms of the specimen. The formed electron gaps are filled with electrons derived from a higher energy level of the same atom. The difference between the two electron energy levels is emitted as x-rays and is specific for the elements. The energy of the x-rays emitted is measured in an x-ray detector allowing identification of the elements and the abundance therefore. EDX mapping can be performed on single spots, lines or a whole area of specimen. In bulky and corrugated specimens like cells or tissues, EDX analysis is restricted to qualitative measurements.

2.5.4 X-Ray Diffraction Analysis (XRD) [15]

XRD is the primary tool for investigating the structure of crystalline materials, from atomic arrangement to crystalline size and imperfections. XRD analysis usually provides measurements of parameters; analysis of solid and liquid samples, reflection, transmission or capillary geometry in-situ high temperature and reactive environment, orientation or texture data, grazing incidence and reflectometry.

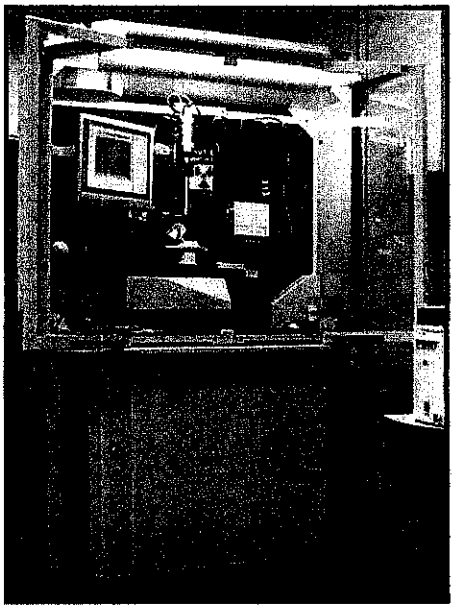


Figure 2.5: X-Ray Diffraction (XRD) Equipment

Applications of XRD analysis include:

- Nanomaterials (phase composition, crystallite size and shape, lattice distortions and faulting, composition variations and orientation)
- Catalysts (for nano-materials with monitoring of structure throughout manufacturing and use to develop structure property relationship)
- New materials development
- Polymers and Composites (crystalline form, crystallinity, crystalline perfection, orientation)
- Pharmaceuticals and Organics (polymorphs, crystallinity and orientation)

2.6 Results from Past Researches [6]

Studies about preparations and characterizations of Co/SiO_2 catalysts for Fischer Tropsch Synthesis (FTS) have been conducted before, mainly about nano-sized cobalt crystallites, its dispersions and reducibility and surface sites. Those studies are carried out by researches especially from Europe countries. Related results from their findings are shown below.

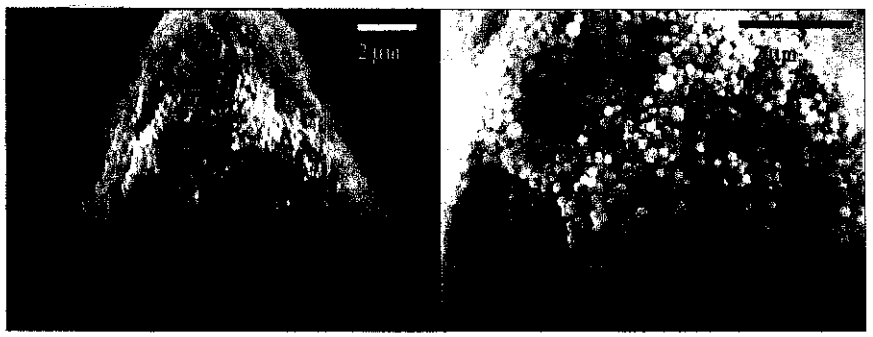


Figure 2.6: Scanning Electron Microscope (SEM) images of the synthesized silica spheres

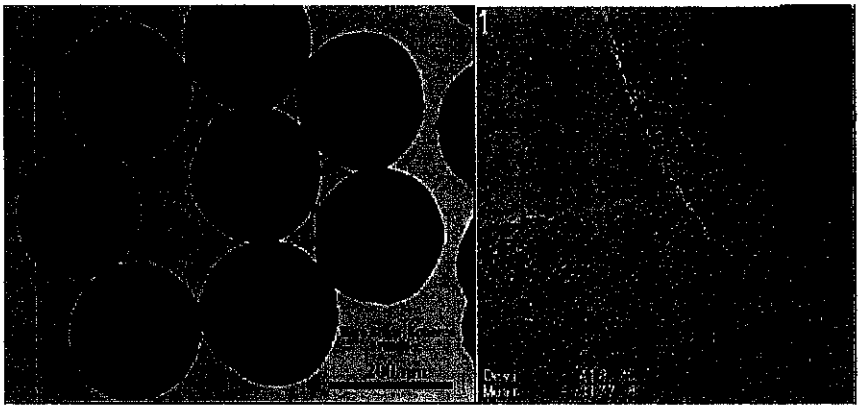


Figure 2.7: Transmission Electron Microscope (TEM) images of the synthesized silica spheres

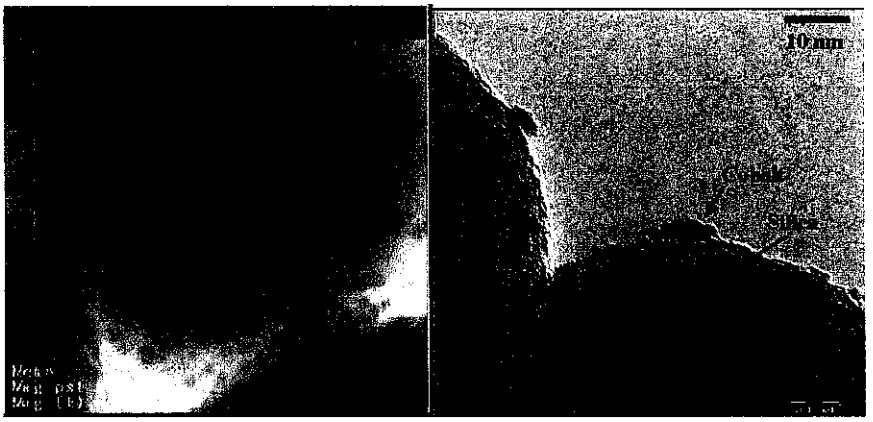


Figure 2.8: Transmission Electron Microscope (TEM) images of 5wt% Co/SiO_2 by ammonia deposition method

CHAPTER 3
METHODOLOGY

3.1 General

The experimental methodology of the project is divided into two main parts, the catalyst preparation and catalyst characterization. The first part involves preparation of silica support and the cobalt catalyst on the silica support, Co/SiO_2. For Co/SiO_2 preparation, the manipulated variable is the loading of cobalt on the silica support. Three values have been identified, 2 wt% Co/SiO_2, 3 wt% Co/SiO_2 and 5 wt% Co/SiO_2. All three types of catalysts will be prepared using ammonia deposition method and the impregnation method.

The chemicals involved in the preparation of the silica support and catalysts are: [3]

i. Ammonium Hydroxide, NH_4OH (25% v/v)
ii. Absolute ethanol (99%)
iii. Tetraethylorthosilicate, TEOS (98%)
iv. Cobalt (II) Nitrate, $Co(NO_3)_2.6H_2O$

Firstly, it is required to determine the weight of $Co(NO_3)_2.6H_2O$ to be used to produce Co/SiO_2 at different loadings. This procedure involves backward calculation whereby the loading is set first before knowing the exact weight of $Co(NO_3)_2.6H_2O$ to be used. Example of calculations to prepare a 3 wt% Co/SiO_2 catalyst is shown below:

Molecular weight of $Co(NO_3)_2.6H_2O$ = 58.9 + 2(14 + 48) + 6(18)

= 290.9

Fraction of cobalt = 58.9 / 290.9

By setting a constant silica weight at 0.5 g, the desired weight of cobalt for 3 wt% loading is determined by:

3 / 97 x 0.5 g = 1.5 / 97 (weight of cobalt required to get a 3 wt% loading)

Weight of $Co(NO_3)_2.6H_2O$ to be used = 1.5 / 97 x 290.9 / 58.9

= 0.08 g

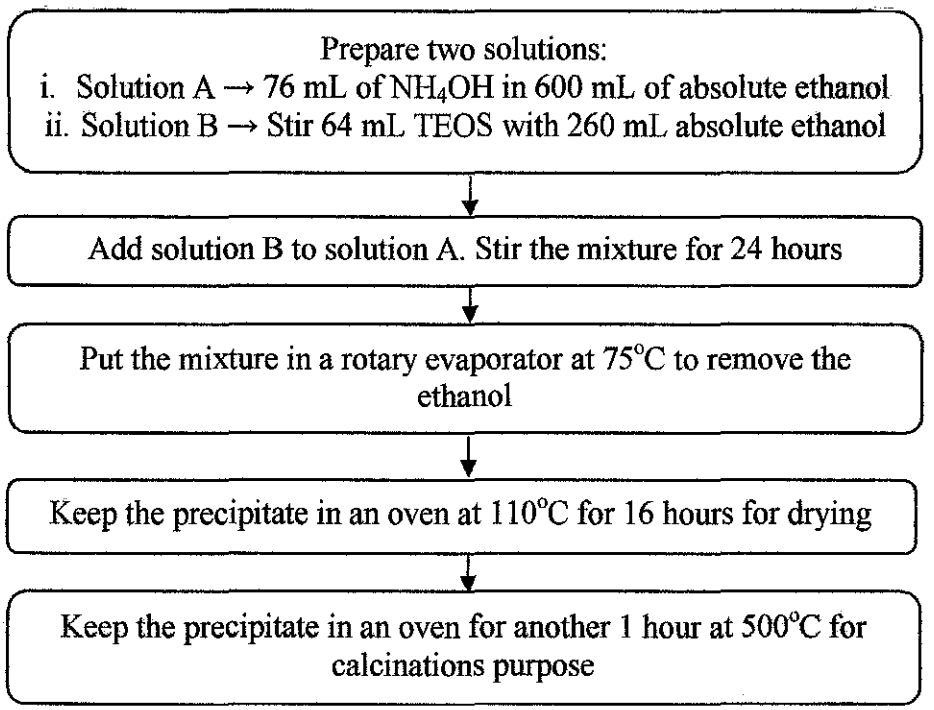
Summary of the calculations is shown in table below:

Table 3.1: Summary of result from metal loadings calculations

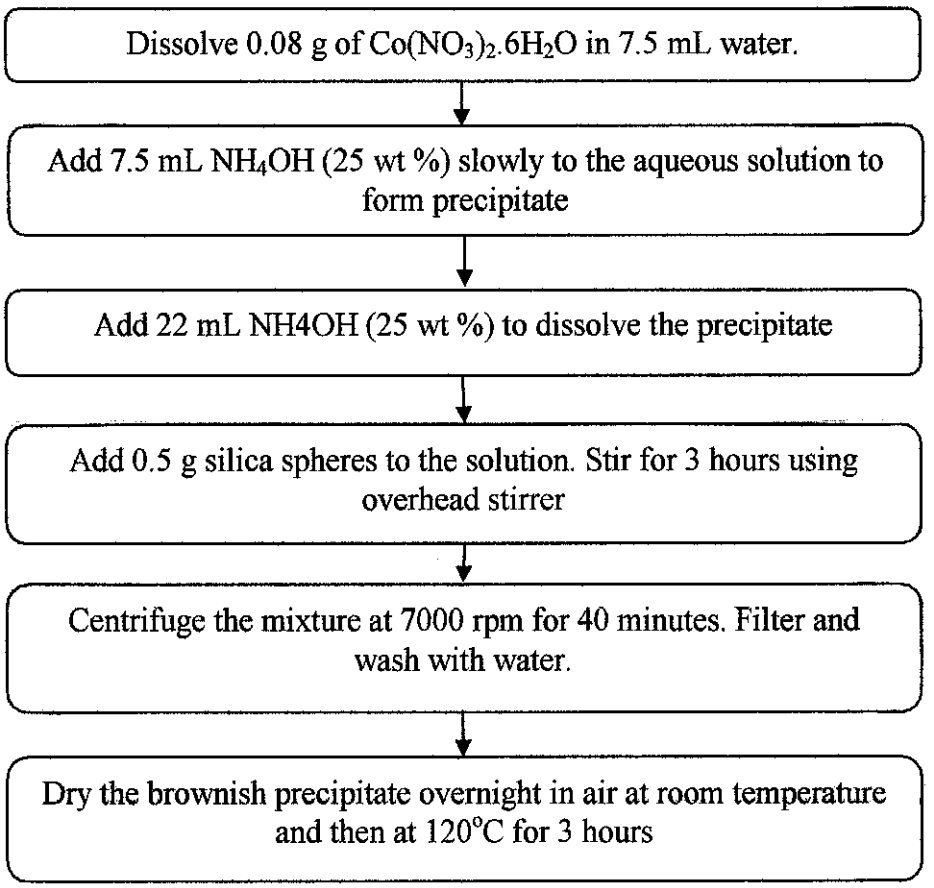
Loading [wt%]	**Weight of $Co(NO_3)_2.6H_2O$ [gram]**
2	0.05
3	0.08
5	0.13

3.2 Catalyst Preparations

3.2.1 Preparation of Silica Support

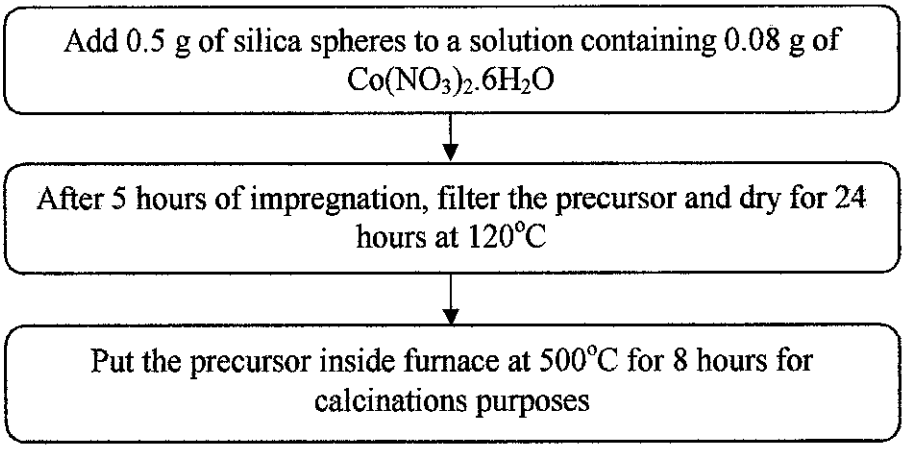


3.2.2 Ammonia Deposition Method (3wt% Co/SiO_2)



The procedures are repeated at different weight of $Co(NO_3)_2.6H_2O$ to get different cobalt loading on the catalysts.

3.2.3 Impregnation Method (3wt% Co/SiO_2)



The procedures are repeated at different weight of $Co(NO_3)_2.6H_2O$ to get different cobalt loading on the catalysts.

3.3 Catalysts Characterizations

After preparing the supported cobalt catalysts at different loading, the sample of each catalyst is sent for characterization to observe its physical properties. Characterizations involve Scanning Electron Microscope (SEM), Energy Dispersive X-Ray (EDX), X-Ray Diffraction (XRD) and Transmission Electron Microscope (TEM). The results from the characterizations are explained further in the next chapter.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Preparation of Silica Spheres

Observations:

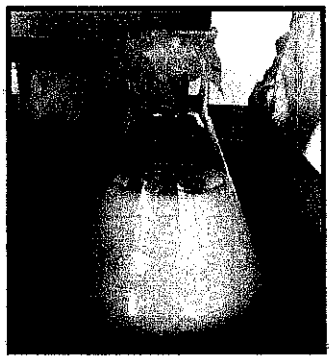


Figure 4.1: Milky white solution after 24 hour stirring

Figure 4.2: Ethanol removal by rotary evaporator

Figure 4.3: Sample put inside oven for drying

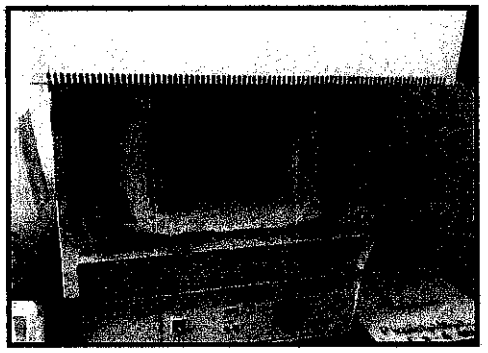


Figure 4.4: Sample put inside furnace for calcinations

Results:

i. Weight of silica after rotary evaporator = **18.8109g**

ii. Weight of silica sphere after drying process inside oven = **17.2926g**

iii. Weight of silica sphere after calcinations inside furnace = **15.9002g**

Figure 4.5: Silica was white in colour after drying

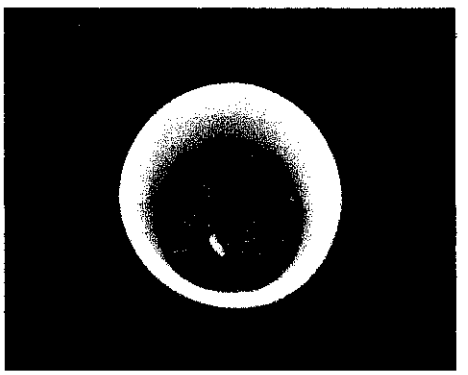


Figure 4.6: Brown silica produced after calcinations

Discussions:

The preparation of silica was conducted by following the Stober method. The final silica produced is desired to be nonporous with BET surface area of less than $100m^2/g$. This is in order to provide a good metal attachment to the silica support when the catalyst preparations take place. The silica must be in white colour after calcinations finished.

Variables like the chemical purity, stirring speed, drying and calcinations temperature need to be put into consideration during the silica preparation. Stirring is important after the absolute ethanol, ammonia solution and TEOS are mixed together to make the mixture homogeneous. A slow stirring speed may result in lower BET surface area. Also the temperature during drying (120°C) and calcinations (500°C) are already set to give optimum results to the removal of water and ammonia from the silica.

The procedures and results stated above are meant for the first attempt of the preparations. For this attempt, the procedures are followed exactly as the Stober method. During stirring of mixture, the beaker was cover with the parafilm. The speed of the stirring is unknown because there was no exact indication at the stirrer used. White silica was produced after 16 hours of drying inside oven. However, after the calcinations process took place, the silica was not white, but in brown colour.

During the calcinations, the silica was placed inside a crucible. Since the silica was in white colour until after drying, thus the changes in final colour might be due to contaminations from the crucible itself. Another assumption made was the contamination was because the beaker was covered while stirring of mixture. When stirring, the mixture, especially absolute ethanol evaporated because of the stirring effect and since the beaker was covered, the absolute ethanol might condensed back into the mixture and become contaminant. The sample of silica from the first attempt was not sent for BET analysis because the final colour itself was already questionable.

The silica preparations continued in the second attempt with aimed to get white silica after calcinations. This time, the beaker was not covered during stirring stage at slow speed. The purpose is to allow efficient evaporation of absolute ethanol without condensed back into the beaker. Other procedures were followed as the first attempt. Before the silica was put in the crucible for calcinations, the crucible was first cleaned properly and put inside furnace at 550°C to remove all contaminants in it. After calcinations for one hour, the final silica of the second attempt was also in brown colour, like the first attempt. Since the crucible was already properly cleaned, the cleanliness issue might not be the problem here. It seemed like the silica was overheated during calcinations until it changed colour. The sample was also not sent for BET analysis.

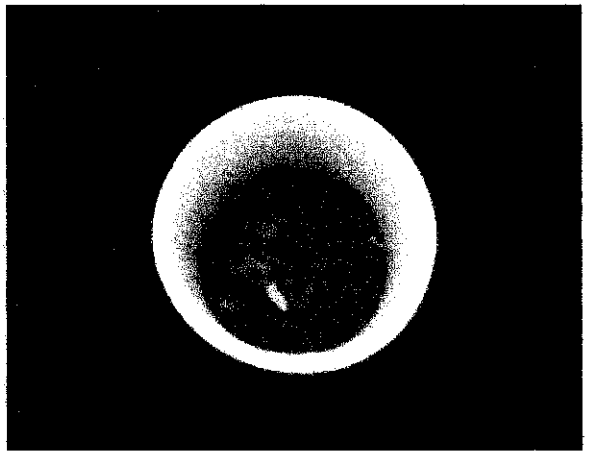


Figure 4.7: Brown silica after second attempt

Third attempt was conducted by following exactly the method done by a research officer before. The procedures were the same as the Stober method, only which the research officer put a time delay between after stirring and drying by rotary evaporator. The reason was to allow proper mixing of the chemicals in the mixture even after stirring. The delay time was 24 hours and the final BET obtained of silica obtained by the research officer was $12m^2/g$. By delaying the time, the white silica was obtained after drying, just like the previous attempts. After calcinations, the final colour of the silica was still not white, but brown. The delay time was not an issue. Only two variables now that contribute to the brown colour; contaminants from the crucible or/and furnace and the calcinations temperature or/and time which might cause excessive heating to the silica. The sample was not sent for BET analysis.

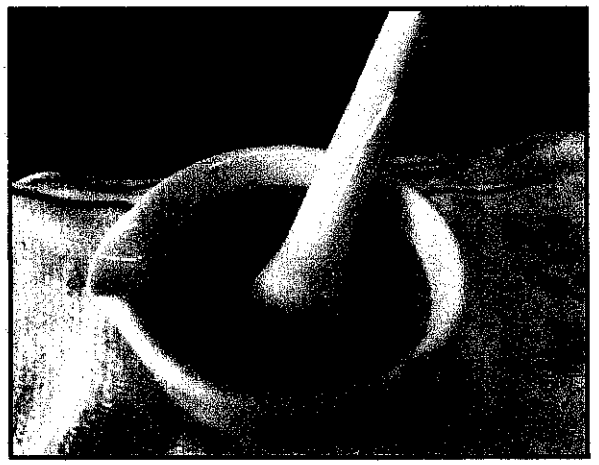


Figure 4.8: Brown silica after third attempt

During the fourth attempt of the silica preparation, the two variables stated above are put into considerations. The procedures are followed as stated in the Stober method with no delay time between after stirring and drying by rotary evaporator. For the attempt, the furnace temperature is monitored during calcinations. The silica was calcined at 500°C for one hour. After one hour, the sample was not straight away taken out from the furnace, but it was left inside there until the furnace temperature decreased to 250°C. In the attempts before, the samples were straight away taken out after one hour. There might be possibility of sudden cooling of the sample when exposed to the ambient condition, which might have changed its colour. After temperature reached 250°C, the sample was taken out and this time again the colour

was still not white. It was 10% brown and 90% white. Assumption of sudden cooling effect was wrong then. The sample was not sent for BET analysis.

Figure 4.9: Almost pure white silica from fourth attempt

The fifth attempt of silica preparations took place with focus now put on the contamination issue at the crucible. This time, different type crucible was used and the sample was put inside two dishes and crucibles during drying and calcinations. The Stober method was still followed. The final silica produced was purely white and it was sent for BET analysis. Result gave a BET surface area of 198m^2/g, which is still undesirable. However, the good news was that proper way to produced white silica is identified and only variables like the stirring speed now need to be considered in order to get a good BET analysis result.

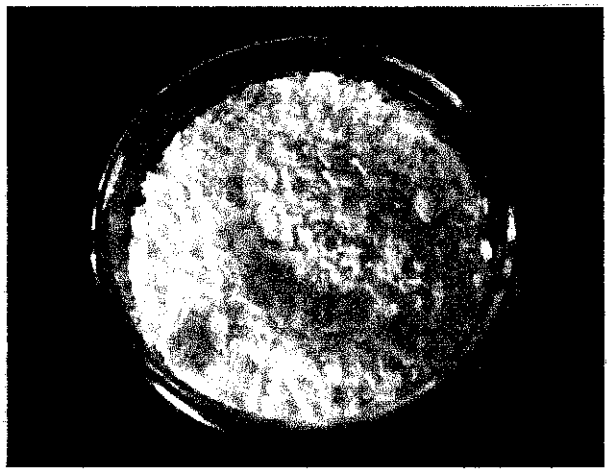


Figure 4.10: The white silica produced in the fifth attempt

Due to time constraint, a good sample of silica could not be produced. The author was allowed to used the sample prepared by a research officer with BET surface area of 61m^2/g. The results from SEM and BET analysis are shown below:

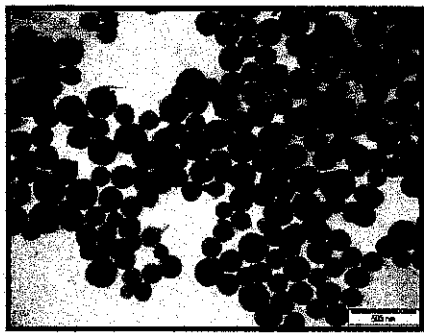


Figure 4.11: Temperature Electron Microscope (TEM) image of silica used for catalyst preparation

BET SURFACE AREA REPORT

BET SURFACE AREA:	61.8923	+/-	0.9020	sq. m/g
SLOPE:	0.089939	+/-	0.001024	
Y-INTERCEPT:	0.000396	+/-	0.000052	
C:	177.640060			
VM:	14.217668	cc/g STP		
CORRELATION COEFFICIENT:	0.99670E-01			

RELATIVE PRESSURE	VOL ADSORBED (cc/g STP)	1/ [VA(Po/P - 1)]
0.0038	9.7306	0.001019
0.0205	11.2564	0.001857
0.0386	12.7508	0.003233
0.0670	14.1205	0.005065
0.0787	14.5700	0.005865

Figure 4.12: Summary from BET surface area analysis

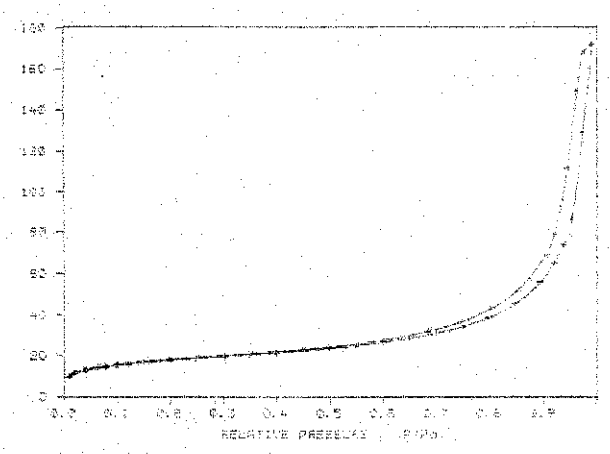


Figure 4.13: Adsorption isotherm obtained from BET analysis of the silica

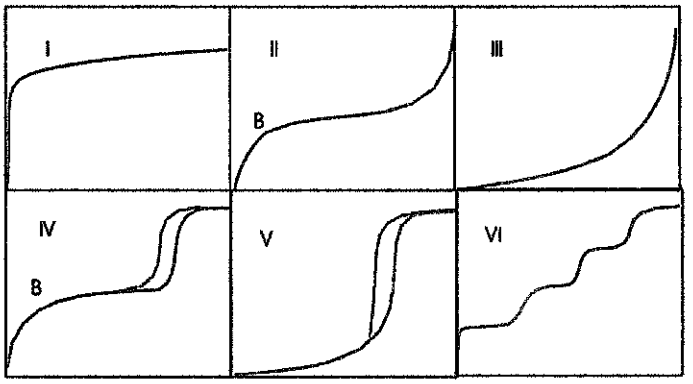


Figure 4.14: Type of adsorption isotherm curves

Adsorption isotherms can be classified in six types according to IUPAC. The Type I is typically for micro porous solids and chemisorptions isotherms. Type II is shown by finely divided nonporous solids. Type III and Type V are typical of vapors, for example water on hydrophobic solids. Type IV and V feature a hysteresis loop generated by the capillary condensation in mesopores. The rare Type VI, the step-like isotherm, is shown, for example nitrogen in special carbons.

To get nonporous silica, the isotherm obtained should be like the shape of Type II graph. Based on Figure 21, the isotherm is the same as Type II isotherm, thus we can consider the silica produced is nonporous.

Table 4.1: Summary of Attempted Silica Preparations

Attempt	Method	Modification	Result	Status
1	Stober	None	Brown silica produced	Failed
2	Stober	Beaker not covered during stirring	Brown silica produced	Failed
3	Stober	24 hour delay after stirring to allow efficient chemical mixing	Brown silica produced	Failed
4	Stober	Sample left inside furnace after calcinations until temperature dropped to 250°C	90% white and 10% Brown silica produced	Failed
5	Stober	Drying and calcinations inside two dishes and crucibles	White silica produced with BET of 198m^2/g (porous)	Failed

4.2 Catalyst Preparations by Impregnation Method

Observations:

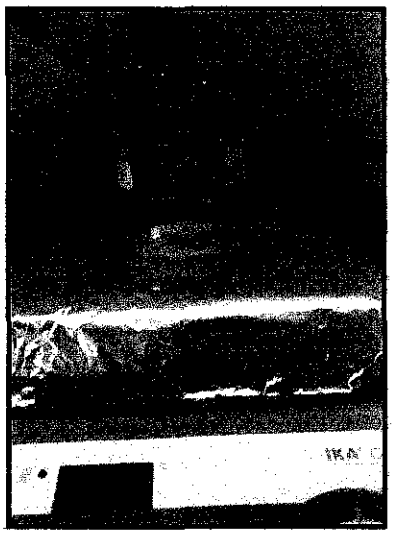


Figure 4.15: Solution being stirred during impregnation

Results:

The final catalyst obtained from impregnation method for 5wt% Co/SiO_2 in black colour. The colour becomes brighter at 3wt% and 2wt% of Co/SiO_2. Before calcinations the colour of the precursors was pink. At first when water was added to solid $Co(NO_3)_2.6H_2O$, pink solution was observed, brighter from higher to lower metal loadings. There no changes in colour during impregnation of the solution until after calcinations when the colour becomes black.

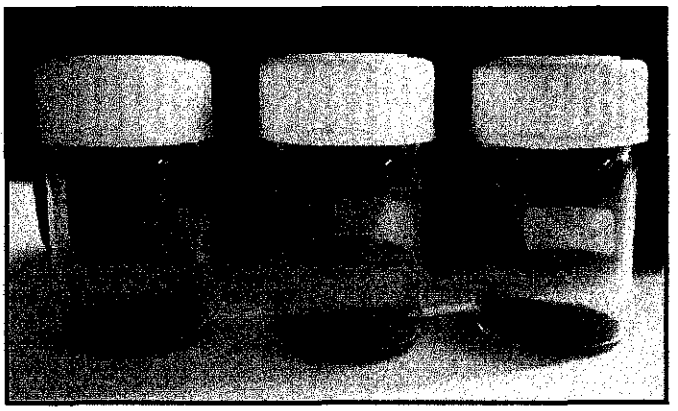


Figure 4.16: Co/SiO_2 catalysts prepared by impregnation method (from left is 2wt%, 3wt% and 5wt%)

4.3 Catalyst Preparations by Ammonia Deposition Method

Observations:

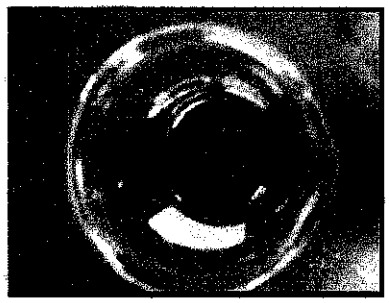


Figure 4.17: Green precipitate formed when ammonia solution was dropped slowly into cobalt (II) nitrate solution

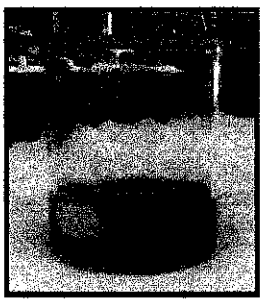


Figure 4.18: Solution formed after excessive ammonia solution added to dissolve the precipitate

Figure 4.19: Stirring of solution using overhead stirrer

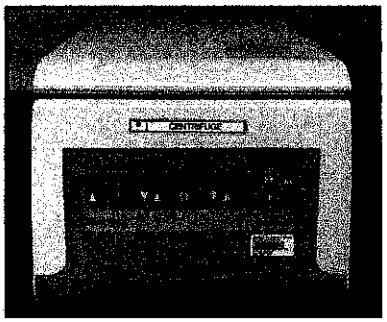


Figure 4.20: Centrifuging process

Figure 4.21: Solution and precursor separated after centrifuging

Figure 4.22: Filtration process

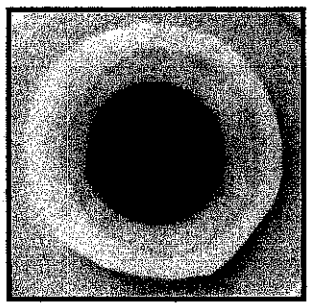


Figure 4.23: 2wt% Co/SiO_2 by ammonia deposition before drying

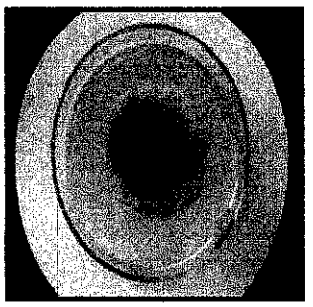


Figure 4.24: 3wt% Co/SiO2 by ammonia deposition before drying

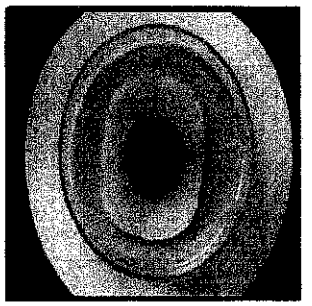


Figure 4.25: 5wt% Co/SiO2 by ammonia deposition before drying

Results:

Preparations of Co/SiO_2 by ammonia deposition method did not involve calcinations process. By observations, the metal was better deposited to the silica by this method as compared to the impregnation method. The colour of the catalyst produced was grey, brighter from 5wt% to 3wt% to 2wt%. Green precipitate was formed when ammonia solution was dropped slowly into beaker containing $Co(NO_3)_2.6H_2O$ solution. After precipitation took place, the reddish brown solution was observed when ammonia solution was added to dilute the precipitate. The colour remained during stirring and centrifugation, only turned to grey after drying at room temperature and 120°C inside oven.

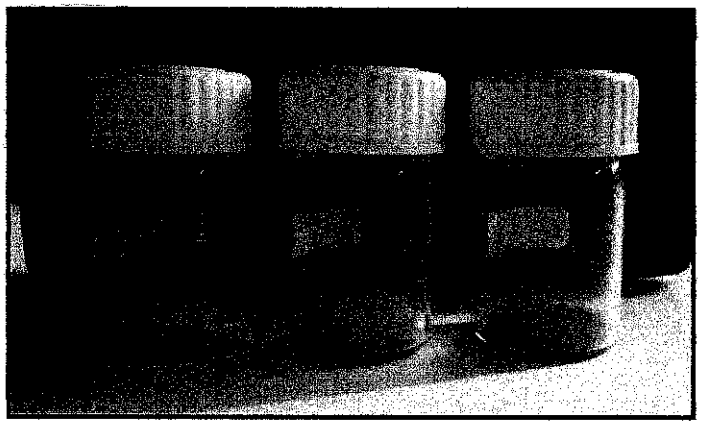


Figure 4.26: Co/SiO_2 catalysts prepared by ammonia deposition method (from left is 2wt%, 3wt% and 5wt%)

4.4 Catalysts Characterizations

The prepared catalysts by impregnation and ammonia deposition methods are characterized to observe their physical properties. The catalysts are characterized by means of Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Energy Dispersive X-ray (EDX) and X-Ray Diffraction (XRD) to study related parameters of the catalysts.

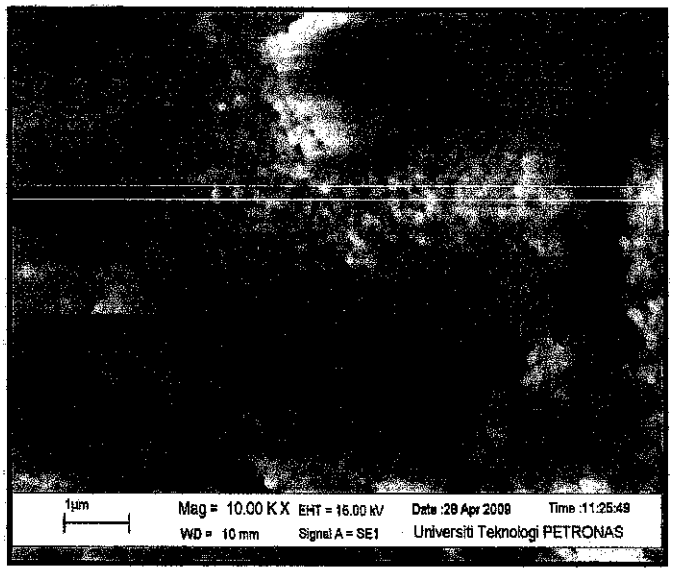


Figure 4.27: Scanning Electron Microscope (SEM) image of 5wt% Co/SiO_2 by impregnation method

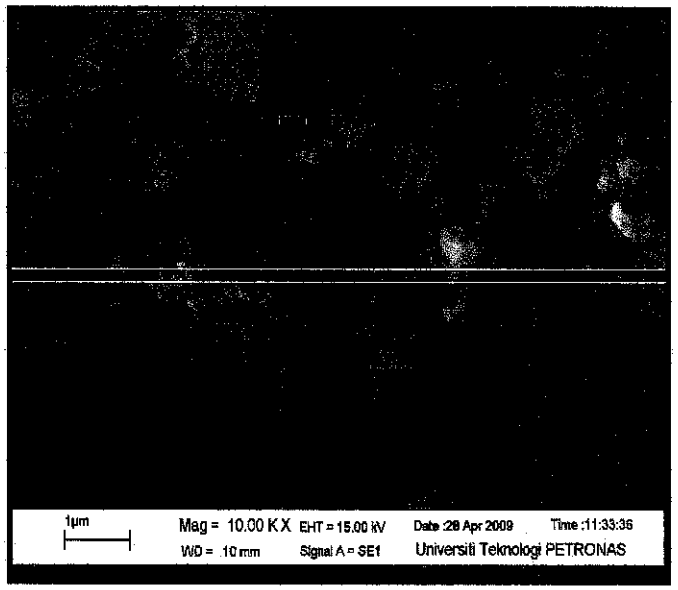


Figure 4.28: Scanning Electron Microscope (SEM) image of 5wt% Co/SiO_2 by ammonia deposition method

Scanning Electron Microscopy (SEM) analysis was conducted on the catalyst sample of 5wt% metal loading in order to observe the physical property particularly the morphology after cobalt was attached onto the silica. Figure 4.27 shows that the silica spheres have formed into clusters (agglomerate) after the catalyst preparations took place by impregnation method. This might be because of thermal effect on the sample especially during calcinations at high temperature. Sample of silica from ammonia deposition method at Figure 4.28 gives better observations whereby there

is only slight agglomerations occur on the silica spheres. The shape of the spheres are consistent indicates that there is no difference in the morphology in the structure. Also, observations from both figures give no evidence of sintering effect at the silica after catalyst preparations. Average diameter for silica spheres from both impregnation and ammonia deposition are 186.5nm and 175.8nm respectively.

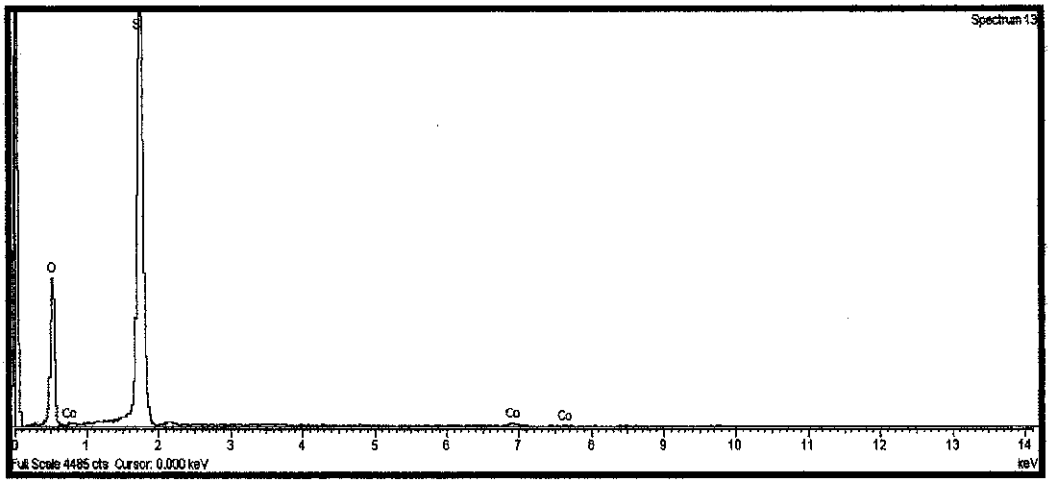


Figure 4.29: Energy Dispersive X-ray (EDX) graph of 5wt% Co/SiO_2 by ammonia deposition method

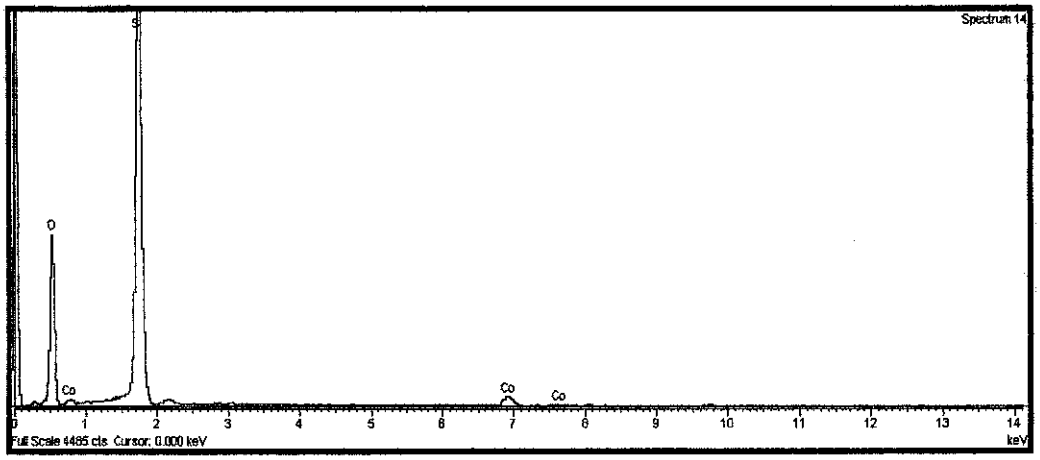


Figure 4.30: Energy Dispersive X-ray (EDX) graph of 5wt% Co/SiO_2 by impregnation method

Energy Dispersive X-Ray (EDX) analysis on both samples shows that there is no unfamiliar elements present in the catalysts. Analysis for sample from impregnation method (Figure 4.30) gives higher peak for cobalt element in the catalysts than sample from ammonia deposition method (Figure 4.29). One indication drawn the

observation is that impregnation method is better than ammonia deposition method in terms of metal loading on silica spheres.

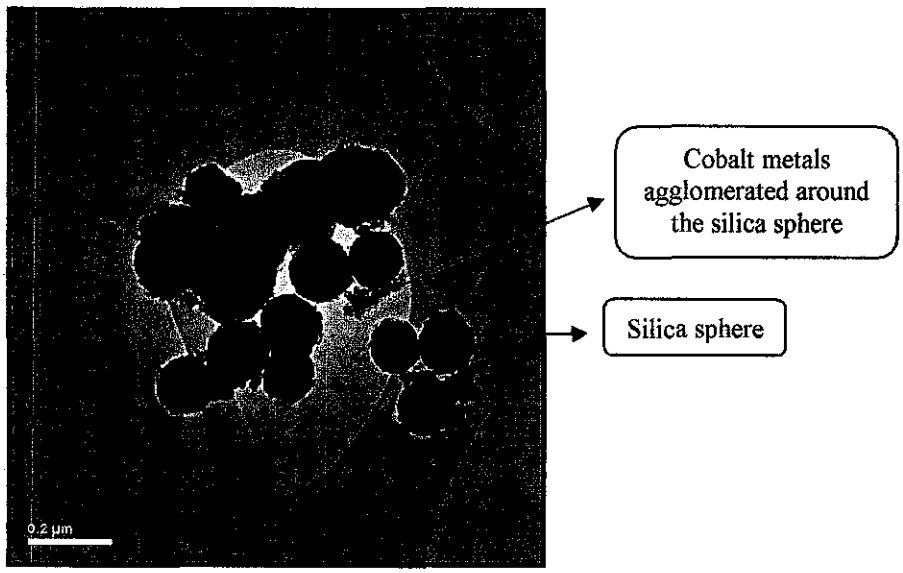


Figure 4.31: Transmission Electron Microscopy (TEM) image of the synthesized silica spheres

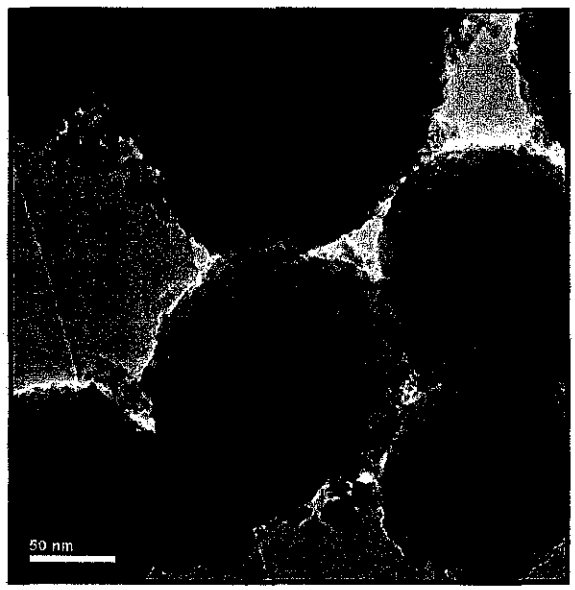


Figure 4.32: TEM image of synthesized silica spheres at different resolution

Figure 4.31 and 4.32 shows TEM images of the synthesized silica spheres. The silica spheres were considered nonporous and smooth surface with slightly sharp edges. The diameter of each silica spheres ranges from 116nm to 183nm.

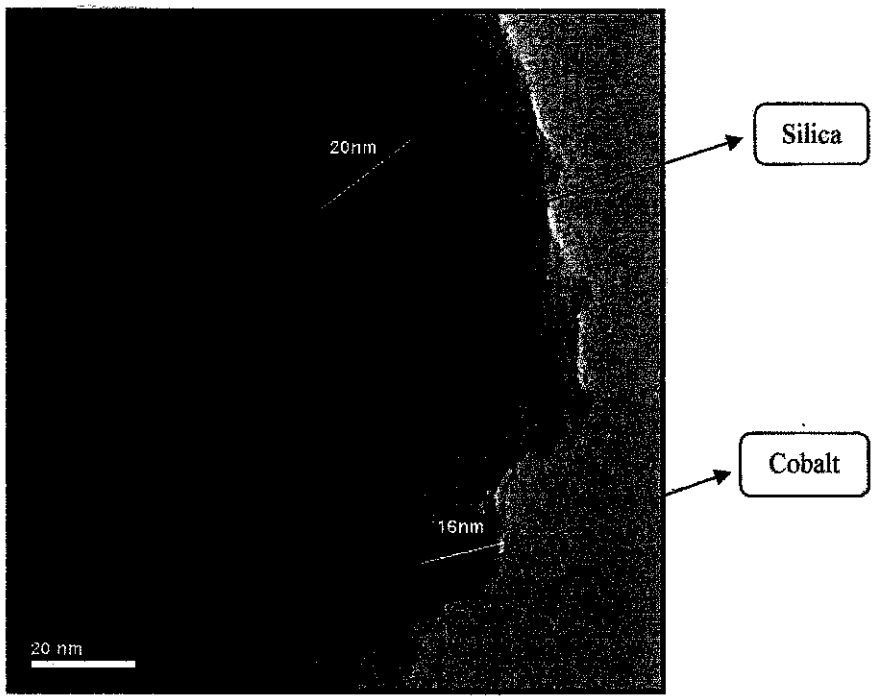


Figure 4.33: TEM image of 5wt% Co/SiO_2 by impregnation method

Figure 4.33 shows the TEM image of the 5wt% Co/SiO_2 spherical model (Co-16nm) catalyst prepared by impregnation, which is, mixing a cobalt nitrate solution with the nonporous silica spheres followed by drying and calcinations. The catalyst model was found to be well-defined with proper attachment of cobalt metal on the silica spheres. However, it seems that the cobalt particle size is bigger than expected (8nm).

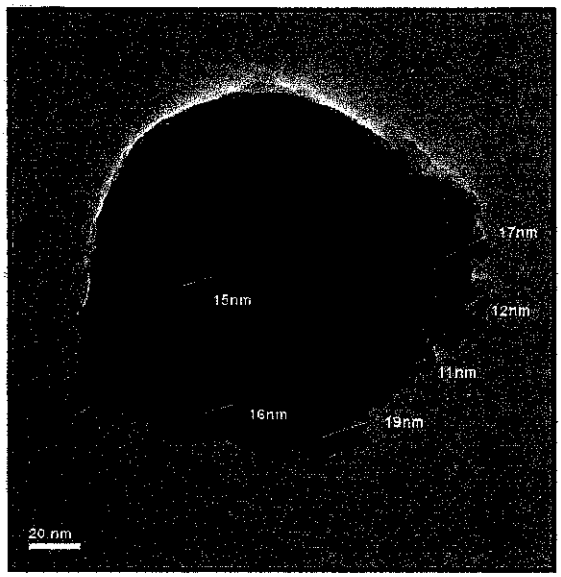


Figure 4.34: TEM image of 5wt% Co/SiO_2 catalyst with different cobalt size attached on the silica

Figure 4.34 gives the representation of cobalt particles at different size attached on a silica sphere after impregnation. The size of the cobalt particles range from 11nm to 19nm diameter and the silica sphere is estimated at diameter of 130nm. There are inconsistencies in the attachment of the metals on the support. It seemed that only one side of a silica sphere is attached with the cobalt metal while the other side not. This might be because of ineffective stirring of mixture during the catalyst preparations. Stirring was conducted by magnetic stirrer on the hot plate and since the volume of mixture was little (7.5mL), the stirring process was not uniform throughout the mixture, causing only certain amount of cobalt particles mixed with the silica spheres. The homogeneous characteristic of the mixture decreased and has resulted in the observations as shown in previous figure.

Measurements of cobalt particles diameter were made manually on the figure as shown before to observe the size distribution of the particle on a silica sphere. This is in order to estimate the average cobalt particle size attached on a silica sphere. A quick statistical representation of the measurement is shown in the next figure.

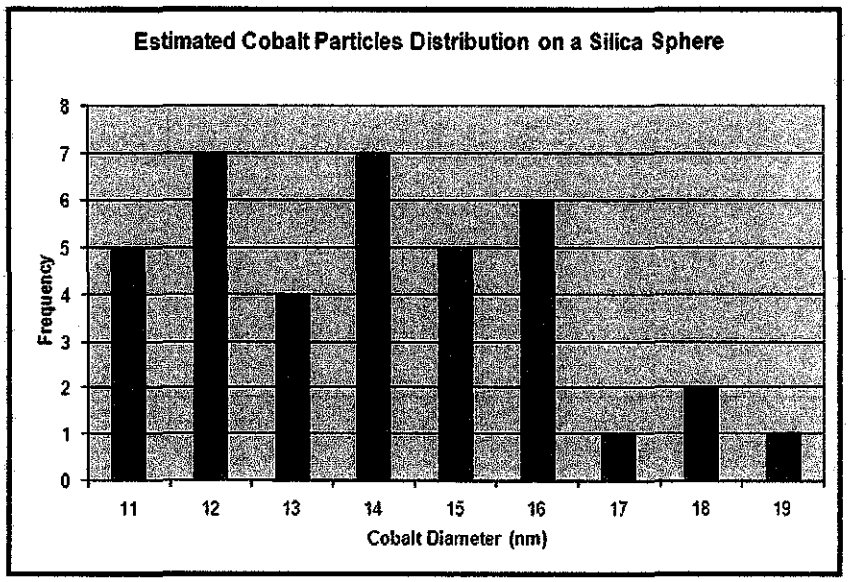


Figure 4.35: Estimated Cobalt Particles Size on a Silica Sphere

From the above figure, it is observed that cobalt particles at a diameter of 12nm and 14nm attached the most on a silica sphere. The distribution is kept in balance at the range from 11nm to 16nm, only a few particles fell on bigger diameter of 17nm to

19nm. The average cobalt diameter from the measurements is estimated at 14nm. However, the measurements done still cannot be considered as accurate since it was based on estimation and did not cover the whole surface of the silica sphere. This is due to inconsistent distribution of cobalt attachment on the silica itself. Also, the measurement was conducted only on a silica sphere. Different ranges of diameter with different average sizes might be obtained at different silica spheres.

Estimation of total cobalt particles attached on a silica sphere is done by assuming the whole surface area of a silica sphere at 130nm diameter is covered with the cobalt particles and also the average cobalt particle diameter is 14nm, as estimated before. The surface area of a silica sphere with diameter of 130nm is calculated as 53093 nm^2. This resulted in a total of about 300 cobalt particles attached on a silica sphere.

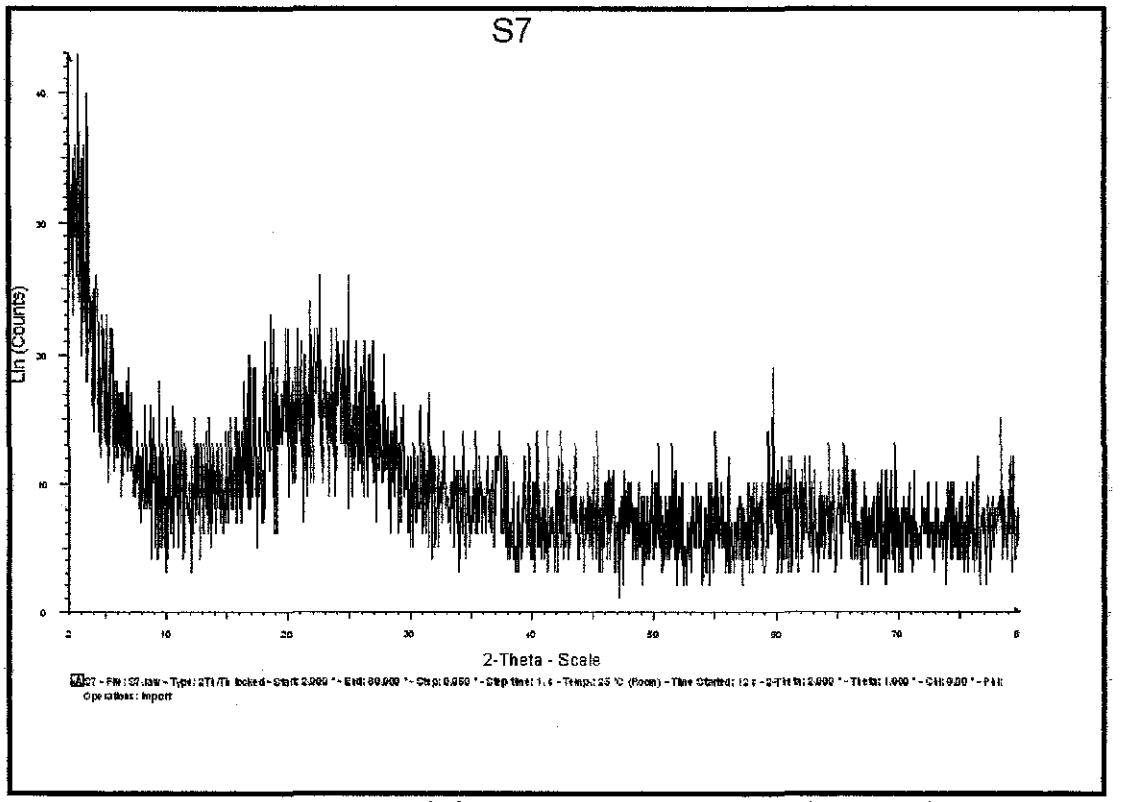


Figure 4.36: XRD result for 3wt% Co/SiO_2 catalyst by impregnation

X-ray diffraction (XRD) analysis is conducted to investigate the structure of crystalline materials, from atomic arrangement to crystalline size and imperfections. This will usually result in either the material is morphous (crystalline) or amorphous. An amorphous material is the kind in which there is no long chain order of the position of the atoms. In principle, given a sufficiently high cooling rate, any liquid can be made into amorphous solid. Cooling reduces molecular mobility. If the cooling rate is faster than the rate at which molecules can organize into a more thermodynamically favorable crystalline state, then an amorphous solid will be formed.

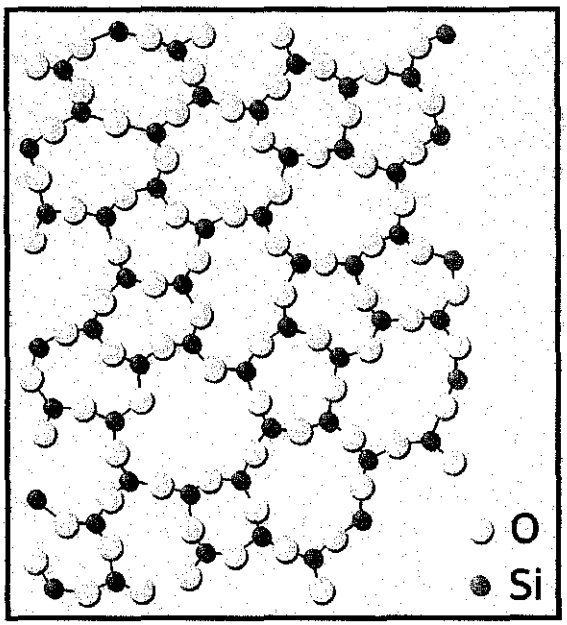


Figure 4.37: The amorphous structure of glassy silica

Theoretically, for structure of silica, as shown in figure 4.37, no long range order present. However, there is local ordering with respect to the tetrahedral arrangement of oxygen atoms around the silicon atoms. Figure 4.36 shows the representation of amorphous nature of the 3wt% Co/SiO_2 catalyst after XRD analysis. The fact that the supported catalyst is largely covered with silica (3% cobalt and 97% silica) makes it hard for the catalyst to be in crystalline structure.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

Reasonable well-defined Co/SiO_2 model catalysts with cobalt loading of 2wt%, 3wt% and 5wt% can be prepared by ammonia deposition and impregnation methods. The silica was first prepared by Stober method to be the support for the catalysts. It took five attempts to prepare the white silica support with BET surface area of 198m^2/g. Different silica supports that have better BET surface area (61m^2/g) were used during catalyst preparations. There are lots of related variables need to be put into considerations during silica and catalysts preparations. Agglomerates were produced by the silica spheres after impregnation method due to thermal effect during calcinations. Preliminary conclusions are drawn from Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) analysis; there is no difference in terms of morphology of the silica before and after catalysts preparations, no sintering effect after catalysts are prepared and impregnation method gives better metal loadings on silica as compared to ammonia deposition method. Transmission Electron Microscopy (TEM) analysis conducted on sample of 5wt% Co/SiO_2 catalyst by impregnation method yield an estimated average of cobalt particles with 14nm diameter attached on a silica sphere. X-ray Diffraction (XRD) measurement indicated that the catalyst samples are in amorphous state.

In summary, the first two objectives of this project were successfully conducted, which are to prepare and characterize the supported cobalt catalysts. However, the related correlations between the physical properties of the catalysts and its preparation method could not be achieved since only one sample being sent for TEM analysis.

There are many variables involved in catalyst preparations and each of them has its own effect on the final product regardless of temporarily or in long term. A few recommendations are drawn out from this research project in order to achieve better results in the future:

- ✓ It is important to monitor related variables such as stirring speed; cleanliness of the equipments used the calcinations temperature during silica preparation. This has proven to be major problems during silica preparation stage.

- ✓ The silica support must be put into two separate dishes and crucibles during drying and calcinations processes in order to allow uniform drying and calcinations on the silica.

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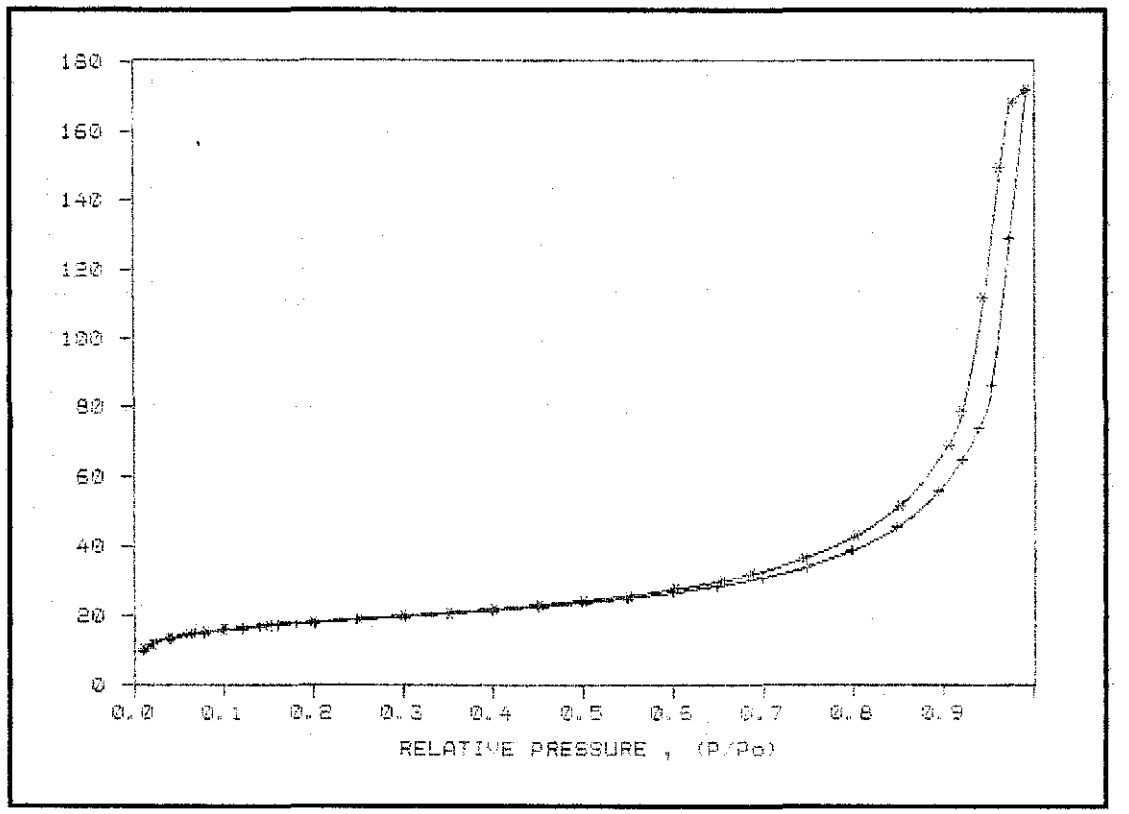
[15] http://www.intertek-cb.com

APPENDICES

APPENDIX A:

BET SURFACE AREA ANALYSIS OF THE SYNTHESIS SILICA SPHERES

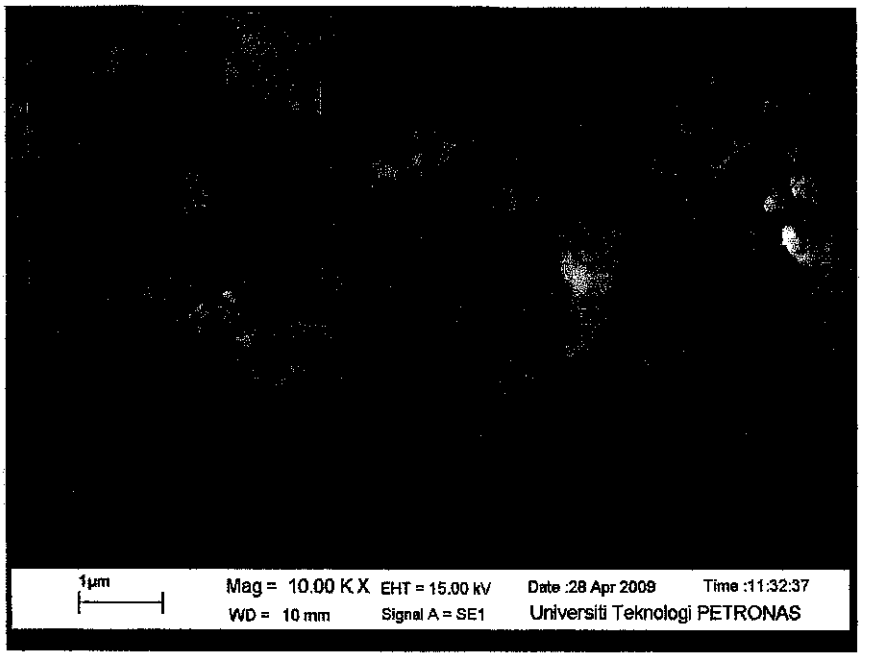


BET SURFACE AREA REPORT

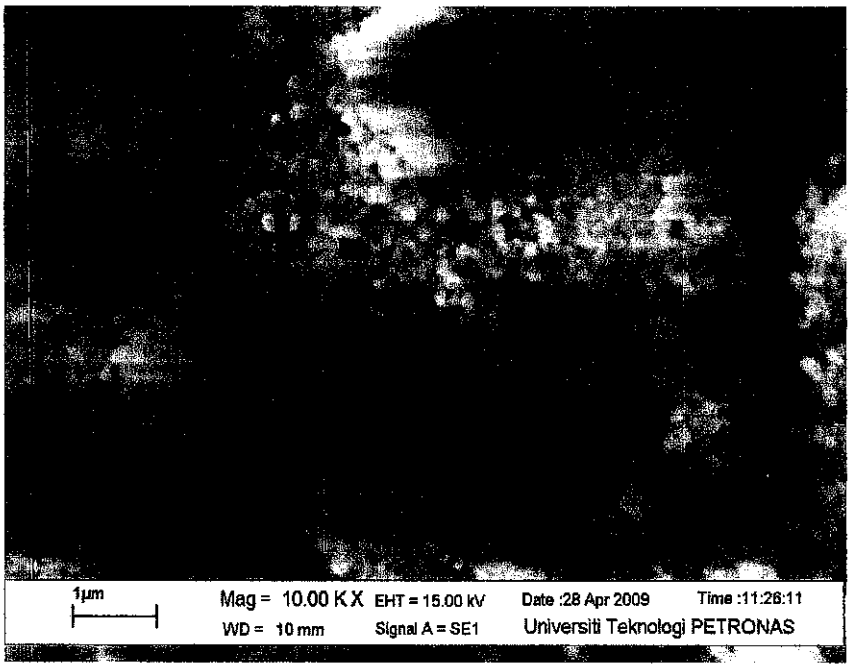
BET SURFACE AREA:	61.8923	+/-	0.9020	sq. m/g
SLOPE:	0.069939	+/-	0.001024	
Y-INTERCEPT:	0.000396	+/-	0.000052	
C:	177.640060			
VM:	14.217668	cc/g STP		
CORRELATION COEFFICIENT:	9.99679E-01			

RELATIVE PRESSURE	VOL ADSORBED (cc/g STP)	1/ [VA(Po/P - 1)]
0.0098	9.7306	0.001019
0.0205	11.2564	0.001857
0.0396	12.7508	0.003233
0.0670	14.1205	0.005085
0.0787	14.5700	0.005865

APPENDIX B:
SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS OF THE CATALYSTS



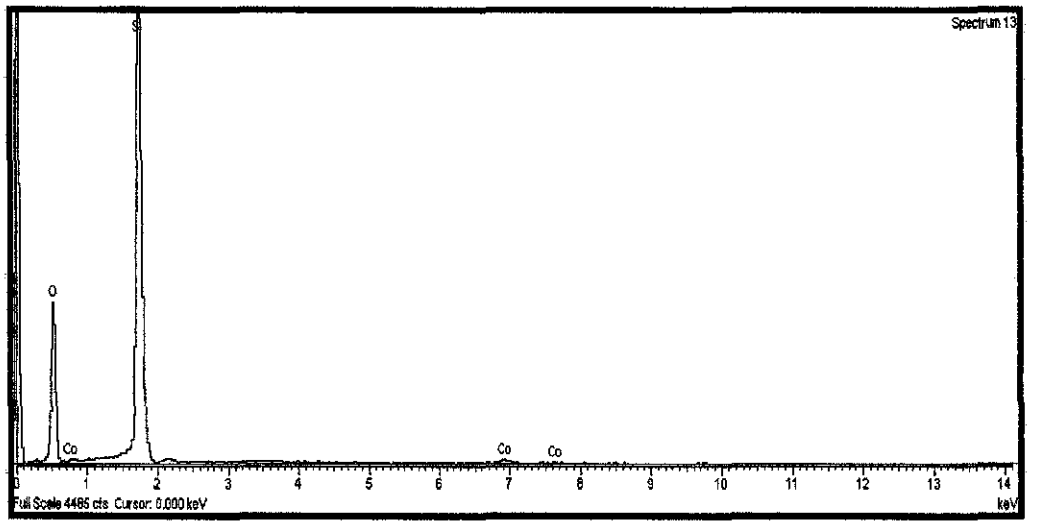
5wt% Co/SiO_2 catalysts by ammonia deposition method



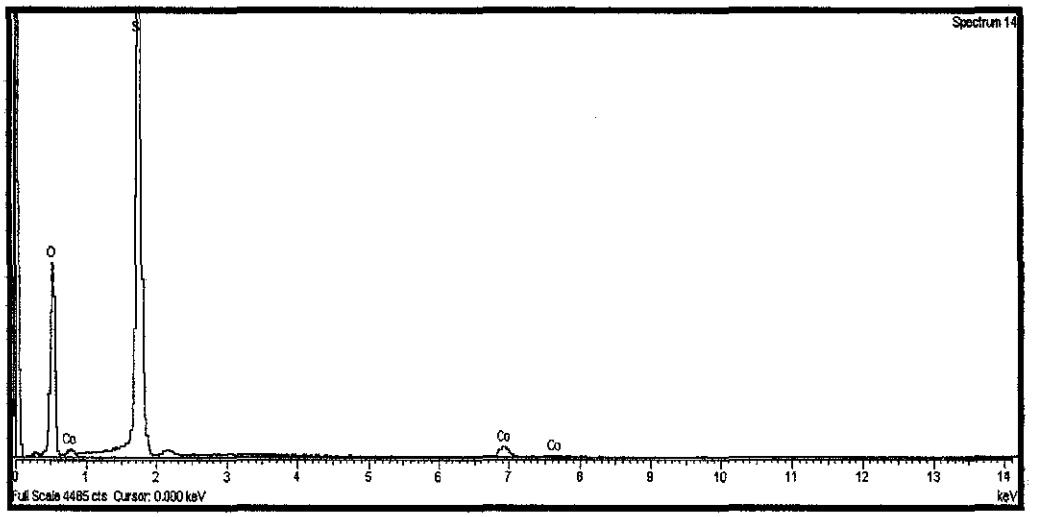
5wt% Co/SiO_2 catalysts by impregnation method

APPENDIX C:

ENERGY DISPERSIVE X-RAY (EDX) ANALYSIS OF THE CATALYSTS



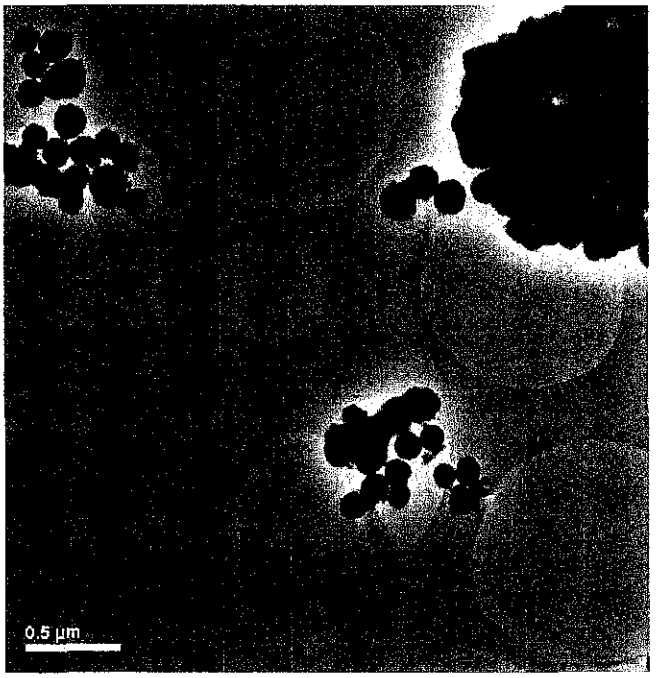
5wt% Co/SiO_2 catalysts by ammonia deposition method

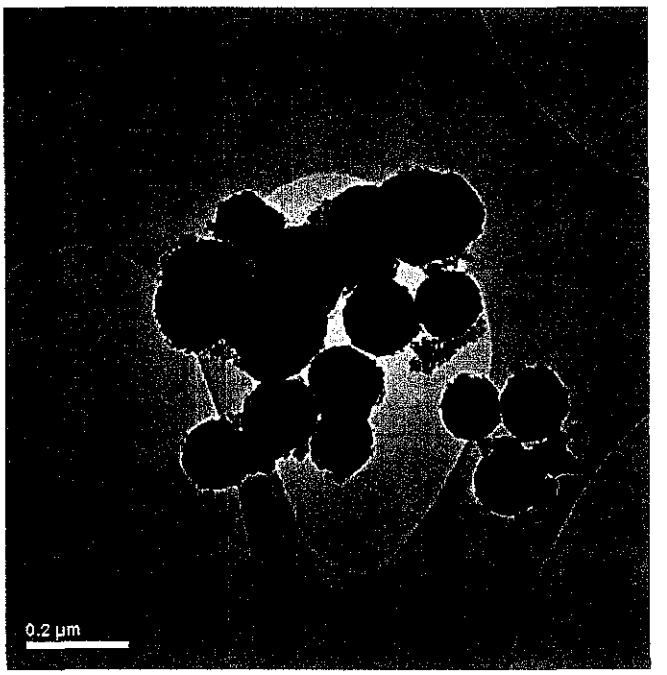


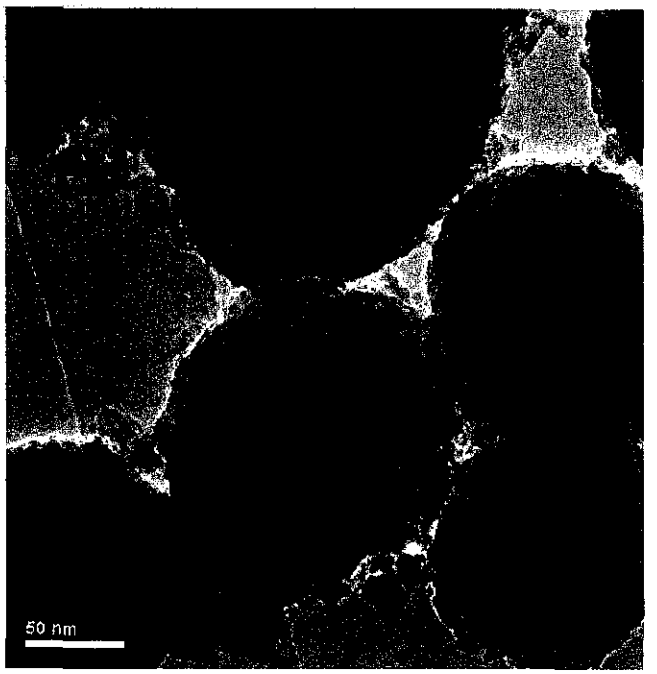
5wt% Co/SiO_2 catalysts by impregnation method

APPENDIX D:

TRANSMISSION ELECTRON MICROSCOPY (TEM) IMAGES OF 5wt% Co/SiO_2 CATALYST BY IMPREGNATION METHOD



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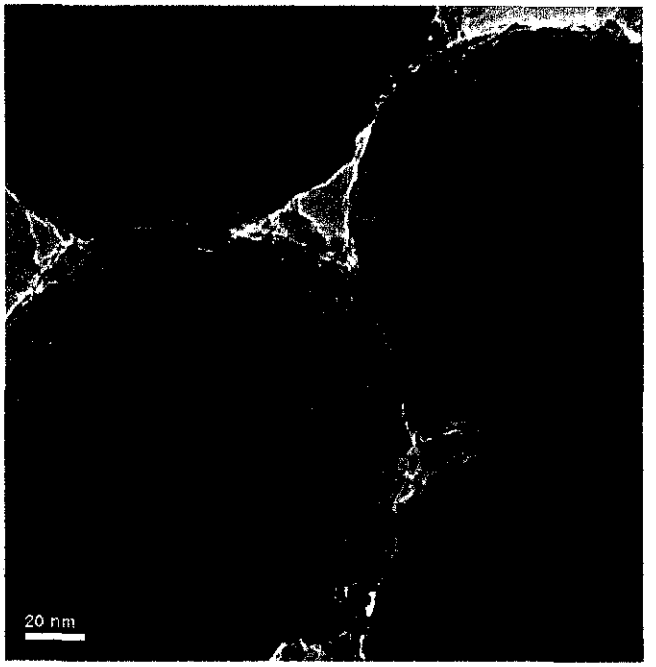
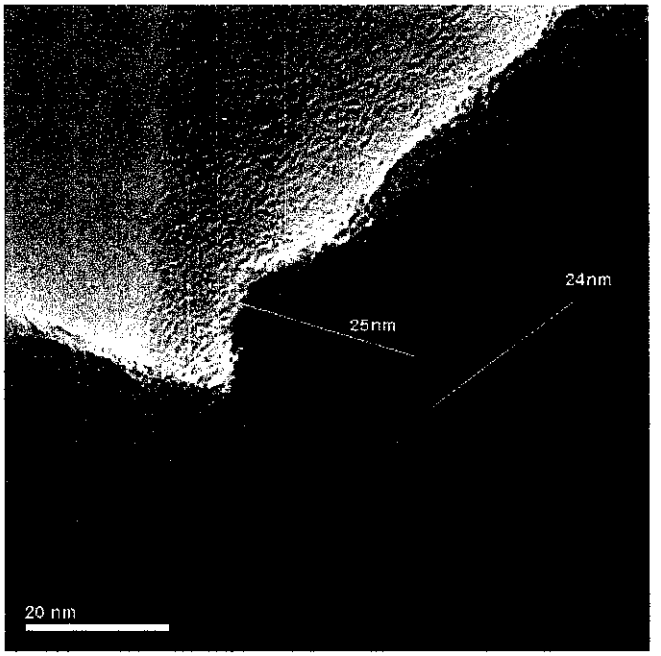
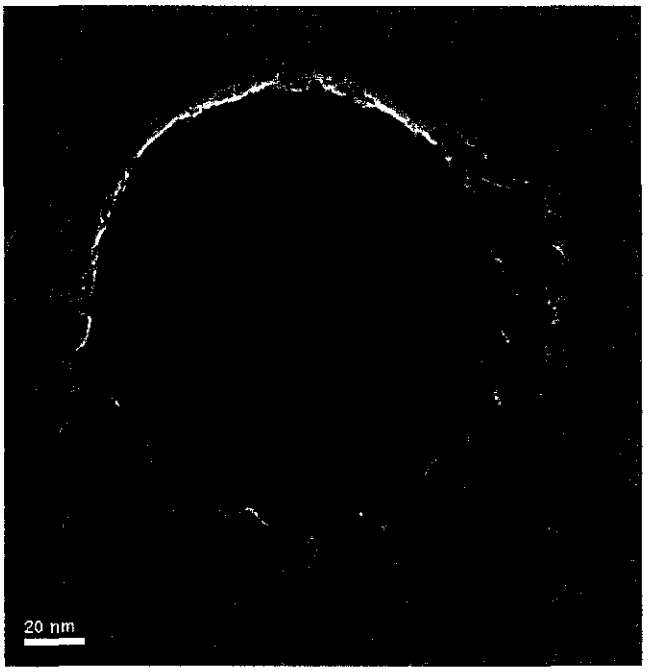

20 nm


24nm
25nm
20 nm


16nm
131nm
31nm
31nm
19nm
27nm
20 nm
38nm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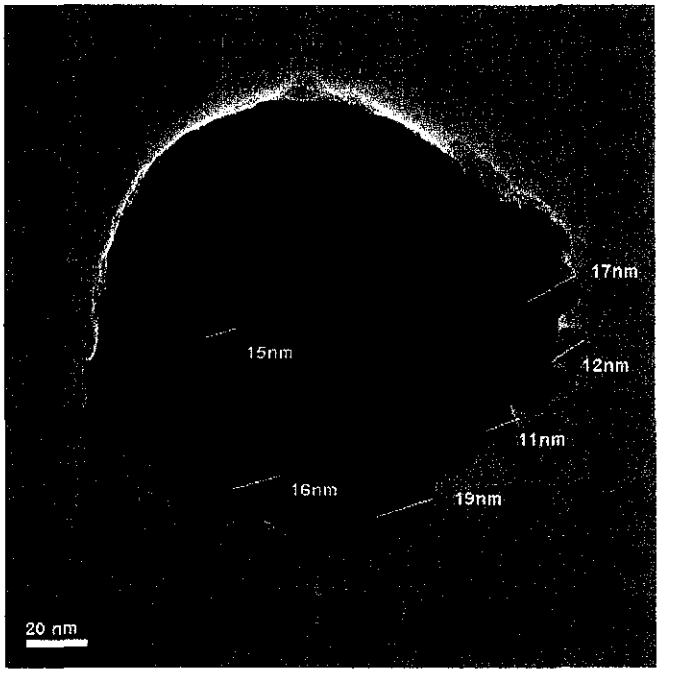
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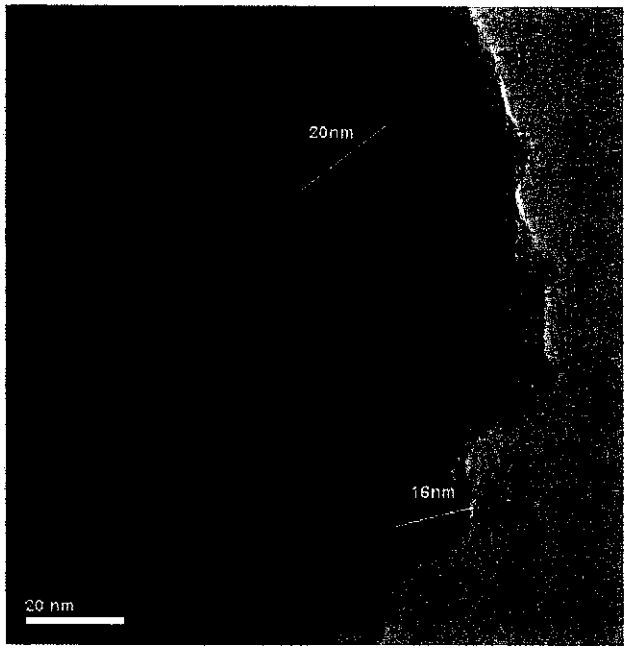
15nm
12nm
11nm
16nm
19nm
20 nm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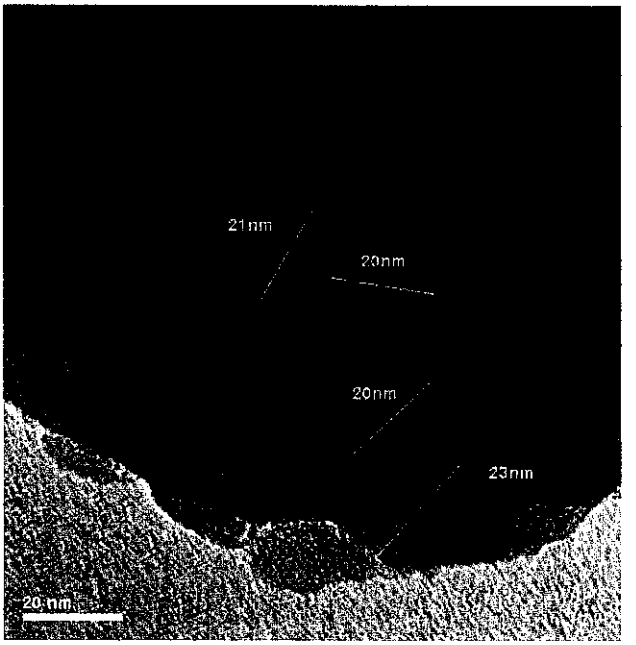
16nm
20 nm


21nm
20nm
20nm
23nm
20 nm

APPENDIX E:

FINAL YEAR PROJECT II GANTT CHART

No	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continue															
2	Submission of Progress Report 1															
3	Project Work Continue															
4	Submission of Progress Report 2															
5	Seminar (compulsory)															
5	Project Work Continue															
6	Poster Exhibition															
7	Submission of Dissertation (soft bound)															
8	Oral Presentation															
9	Submission of Project Dissertation (hard bound)															

	Suggested Milestone
	Process